NUCLEATION AND GROWTH OF TERRESTRIAL BIOGENIC/ANTHROPOGENIC AEROSOLS

Atmospheric Science Program (ASP)

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Introduction

Molecular processes leading to the formation of nano-sized particles are highly complex and often involve the interaction between biogenic organic acids and anthropogenic sulfuric acid. Through novel application of "nucleation theorems" to laboratory measurements of new particle formation carried out at MIT and Texas A&M, we have been able to determine the molecular composition of the critical nucleus (size circa 1nanometer in diameter) the formation rate of which determines the rate of new particle formation[1-3]. Our finding is that just a single molecule of the organic acid together with several molecules of sulfuric acid (from three to eight) and additional water molecules comprise the critical nucleus. From this information we obtained a simple parameterization of the nucleation rate suitable for use in models of atmospheric new particle formation. These results are being applied this year to model field observations of both daytime (sulfuric acid limited) and nighttime (qualitatively different and possibly organics limited) nucleation events.

Approach

The complexity of the molecules involved in these ternary nucleation processes and their interactions prevents the application of classical nucleation theory (CNT) to these systems. CNT is a phenomenological theory that attempts to describe molecular cluster properties in terms of measurable properties of the bulk system: surface tension, density and partial vapor pressures of the species present. Even if the bulk were an effective representation of cluster properties, the needed properties measurements are by and large not available for systems of atmospheric interest. Another approach is needed and for this we use the so-called "nucleation theorem" (NT). Rooted in the law of mass action and principle of detailed balance the NT circumvents the need to apply CNT. The NT is most useful for interpretation of steady-state nucleation rate measurements in terms of molecular occupation numbers for species present in the critical nucleus.

Nucleation Theorem

The nucleation theorem yields optimal coordinates and a multi-linear dependence for the nucleation rate in terms of temperature and multi-component vapor concentrations. Because the measurements of Zhang and co-workers [1-3] are at constant temperature, the present analysis is focused on isothermal conditions and vapor concentration dependence.

$$J = \sum_i J_i = \sum_i \kappa_i \beta_i n(g^*_1, g^*_2, \cdots)$$

Transition state model

equilibrium cluster population

$$\left(\frac{\partial \ln J}{\partial \ln n_i}\right)_{T,\{n_j, j\neq i\}} = g^*_i + \delta_i \rightarrow$$

essentially law of mass action
1st N-theorem

$$\ln J \approx \ln J_0 + \sum_i (g^*_i + \delta_i)(\ln n_i - \ln n_i^0)$$

small kinetic term

nucleus content species i

Nucleation Rate Parameterization [1]

Equation 1 is a parameterization for the total nucleation rate from the combined binary (sulfuric acid-water) and ternary (organic acid-sulfuric acid-water) pathways

$$J_{\text{model}}(x,y) = 10^{-6.58+9.17x} + 10^{-3.67+8.12x+1.86y} \qquad (1)$$

where $x = Log_{10}[H_2SO_4, molecules/cm^3] - 9$ and $y = Log_{10}[Organic\ acid, ppb]$. The structure of Eq. 1 follows from the nucleation theorem. The numerical constants are from a fit of the model to combined laboratory measurements for the binary sulfuric acid-water system and the ternary p-toluic acid-sulfuric acid-water system. The parameterization shows excellent agreement with measurements spanning over 5 orders of magnitude in nucleation rate (Figures 1 and 2 below):

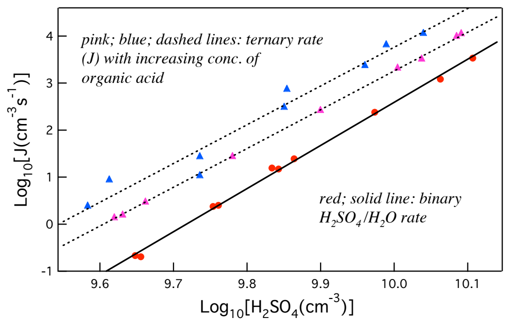


Figure 1. Laboratory measurements show strong linear behavior in nucleation theorem coordinates. Critical nucleus molecular content is obtained from the slopes (8 molecules of sulfuric acid and 1 molecule of organic acid present in the critical nucleus).

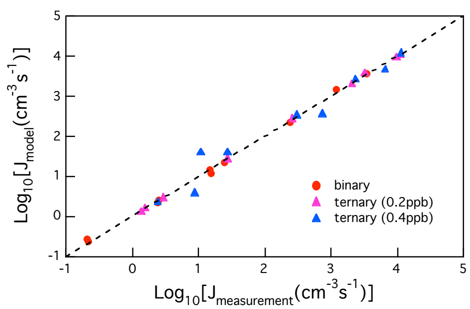
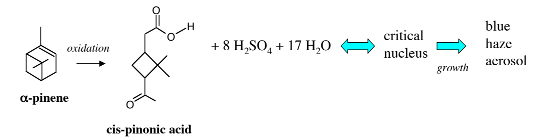


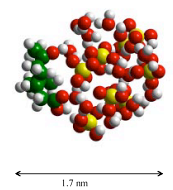
Figure 2. Comparison of parameterized model (Eq. 1) with laboratory measurements of nucleation rate showing superposition of binary and ternary rate measurements on the same plot. The dashed line shows the 1-1 line drawn for comparison. From [1].

CHARACTERIZING THE CRITICAL NUCLEUS OF "BLUE HAZE" [3]

Proposed mechanism (involves both natural and anthropogenic precursors):



CRITICAL NUCLEUS STRUCTURE FROM MOLECULAR DYNAMICS [2]



Nucleus shows clear separation into hydrophobic and hydrophilic parts connected by hydrogen bonds.

Interpretation: CPA leads to stabilization of the sulfuric acid/water complex and enhancement of nucleation rate over the binary rate.

MD simulation of the CPA/ H_2SO_4/H_2O nucleus

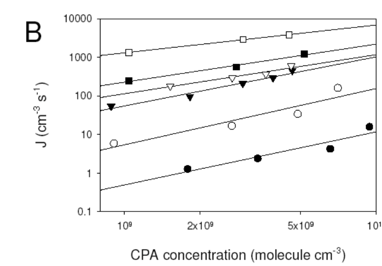


Figure 3. Nucleation rate vs vapor concentration of cis-pinonic acid at several sulfuric acid concentrations and RH=20%. Slope in these NT coordinates shows a single molecule of CPA in the critical nucleus. From [3].

References

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